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ESSENTIAL GUIDES TO METHOD DEVELOPMENT IN EXTRACTION

J. R. Dean, University of Northumbria at Newcastle, Newcastle upon Tyne, UK

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Introduction

Samples for extraction can be broadly categorized as solid, liquid or gaseous matrices. It is obvious that the different methods of extraction of analytes from these matrices will also vary. This guide provides an overview of the different approaches for extraction of analytes from these different matrices.

It is important to consider that extraction is only one part of the sample preparation protocol. Other steps are highlighted in **Figure 1**. A typical solid sample is most likely to be heterogeneous. This is a problem in the analysis, if appropriate steps have not been taken to remove a representative sample using a statistical approach. Failure to do so can make any subsequent extraction and analysis results meaningless.

Also of relevance to any subsequent extraction and analysis is whether the sample has been stored (and preserved, if necessary) in the appropriate manner to prevent losses of the analyte due to degradation and/or adsorption. It is necessary to consider, in the

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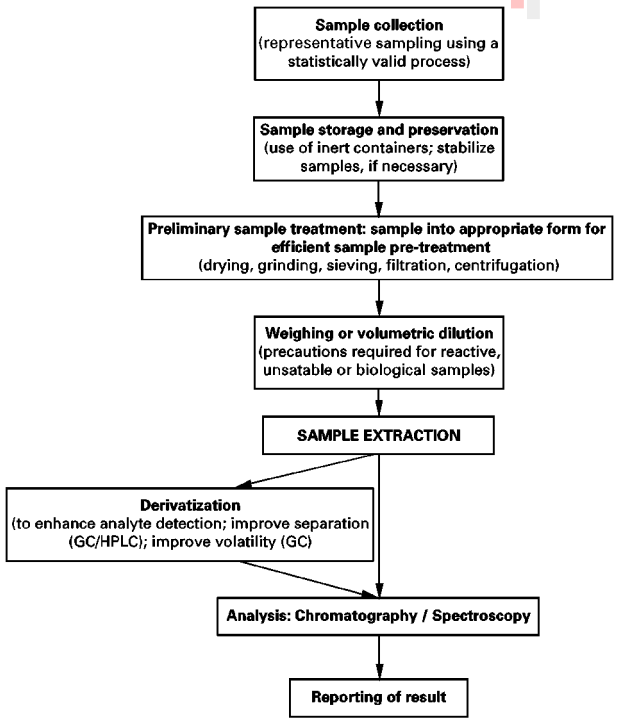
Sample collection
(representative sampling using a statistically valid process)
Sample storage and preservation
(use of inert containers; stabilize samples, if necessary)
Preliminary sample treatment: sample into appropriate form for efficient sample pre-treatment
(drying, grinding, sieving, filtration, centrifugation)
Weighing or volumetric dilution
(precautions required for reactive, unsatable or biological samples)
SAMPLE EXTRACTION
Derivatization
(to enhance analyte detection; improve separation (GC/HPLC); improve volatility (GC)
Analysis: Chromatography / Spectroscopy
Reporting of result

Figure 1 Sample preparation protocol.

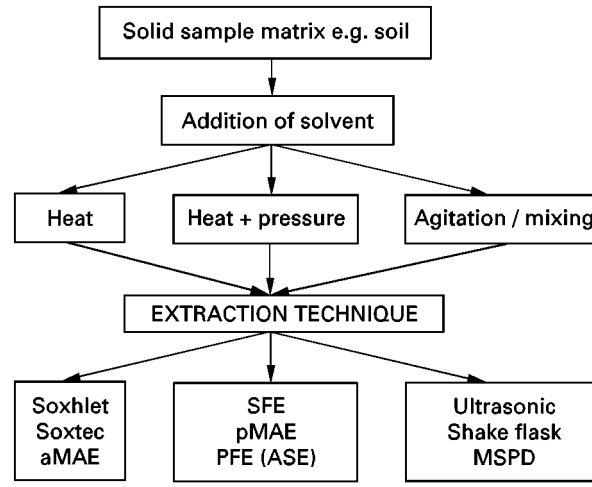

Figure 2 Extraction of analytes from solid matrices.

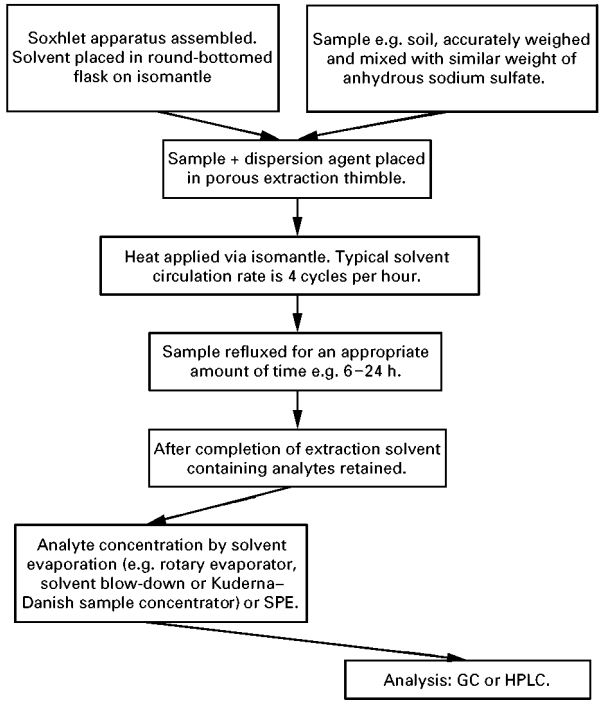
Soxhlet apparatus assembled. Solvent placed in round-bottomed flask on isomantle
Sample e.g. soil, accurately weighed and mixed with similar weight of anhydrous sodium sulfate.
Sample + dispersion agent placed in porous extraction thimble.
Heat applied via isomantle. Typical solvent circulation rate is 4 cycles per hour.
Sample refluxed for an appropriate amount of time e.g. 6–24 h.
After completion of extraction solvent containing analytes retained.
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator) or SPE.
Analysis: GC or HPLC.

Figure 3 Soxhlet extraction.

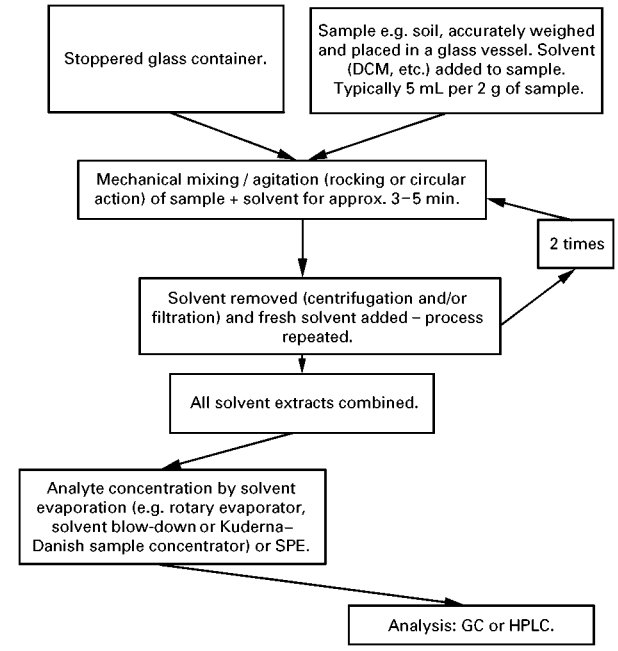
Stoppered glass container.
Sample e.g. soil, accurately weighed and placed in a glass vessel. Solvent (DCM, etc.) added to sample. Typically 5 mL per 2 g of sample.
Mechanical mixing / agitation (rocking or circular action) of sample + solvent for approx. 3–5 min.
2 times
Solvent removed (centrifugation and/or filtration) and fresh solvent added – process repeated.
All solvent extracts combined.
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator) or SPE.
Analysis: GC or HPLC.

Figure 5 Shake-flask extraction.

case of a soil sample, whether it should be dried (volatile analytes may be lost) or extracted in the unadulterated state. If possible, drying is favoured, as the subsequent matrix can be ground and sieved to increase its surface area (smaller particle size).

Solid Matrices

Extraction of analytes from solid matrices can be classified according to the scheme shown in **Figure 2**. The main extraction techniques are Soxhlet extraction, soxtec extraction, supercritical fluid extraction

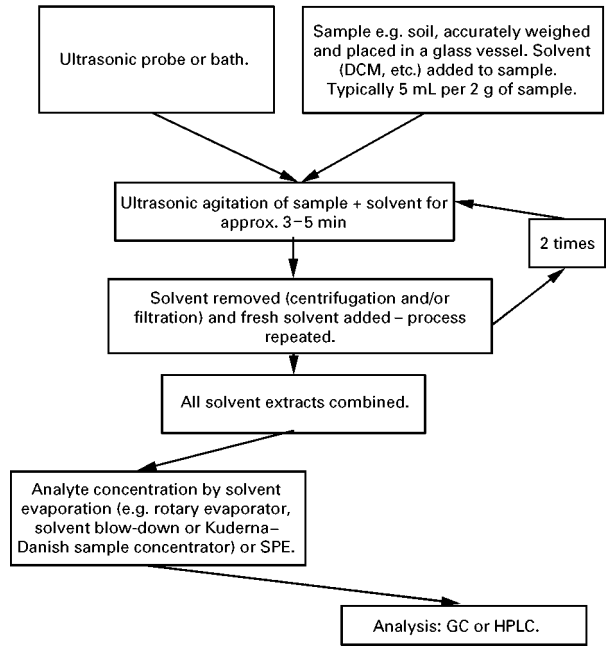
Ultrasonic probe or bath.
Sample e.g. soil, accurately weighed and placed in a glass vessel. Solvent (DCM, etc.) added to sample. Typically 5 mL per 2 g of sample.
Ultrasonic agitation of sample + solvent for approx. 3–5 min
2 times
Solvent removed (centrifugation and/or filtration) and fresh solvent added – process repeated.
All solvent extracts combined.
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator) or SPE.
Analysis: GC or HPLC.

Figure 4 Ultrasonic extraction.

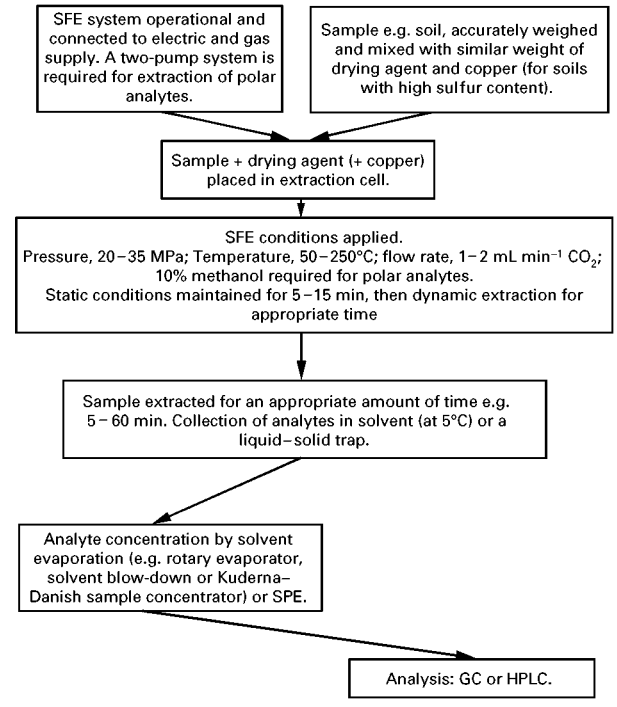
SFE system operational and connected to electric and gas supply. A two-pump system is required for extraction of polar analytes.
Sample e.g. soil, accurately weighed and mixed with similar weight of drying agent and copper (for soils with high sulfur content).
Sample + drying agent (+ copper) placed in extraction cell.
SFE conditions applied.
Pressure, 20–35 MPa; Temperature, 50–250°C; flow rate, 1–2 mL min⁻¹ CO_2; 10% methanol required for polar analytes.
Static conditions maintained for 5–15 min, then dynamic extraction for appropriate time
Sample extracted for an appropriate amount of time e.g. 5–60 min. Collection of analytes in solvent (at 5°C) or a liquid–solid trap.
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator) or SPE.
Analysis: GC or HPLC.

Figure 6 Supercritical fluid extraction.

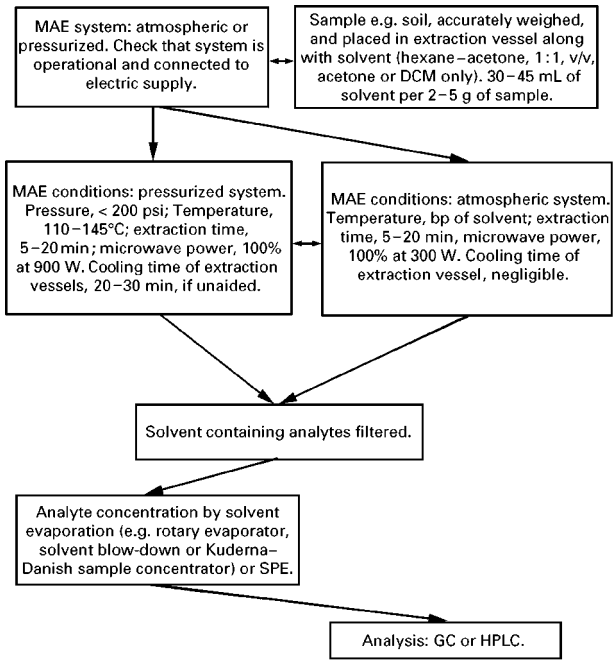
MAE system: atmospheric or pressurized. Check that system is operational and connected to electric supply.
Sample e.g. soil, accurately weighed, and placed in extraction vessel along with solvent (hexane–acetone, 1:1, v/v, acetone or DCM only). 30–45 mL of solvent per 2–5 g of sample.
MAE conditions: pressurized system. Pressure, < 200 psi; Temperature, 110–145°C; extraction time, 5–20 min; microwave power, 100% at 900 W. Cooling time of extraction vessels, 20–30 min, if unaided.
MAE conditions: atmospheric system. Temperature, bp of solvent; extraction time, 5–20 min, microwave power, 100% at 300 W. Cooling time of extraction vessel, negligible.
Solvent containing analytes filtered.
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator) or SPE.
Analysis: GC or HPLC.

Figure 7 Microwave-assisted extraction.

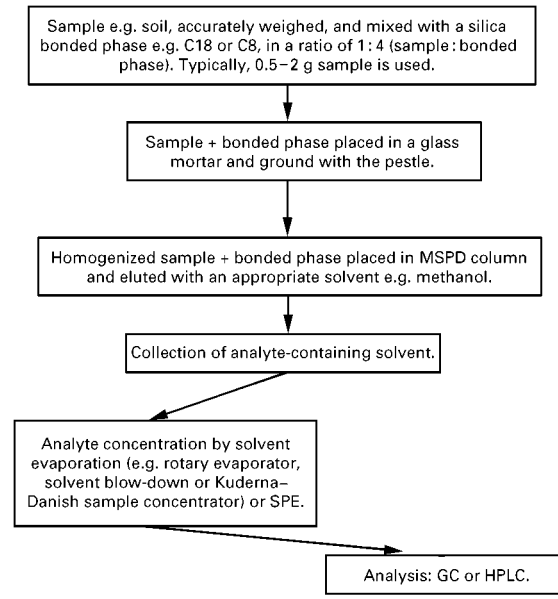
Sample e.g. soil, accurately weighed, and mixed with a silica bonded phase e.g. C18 or C8, in a ratio of 1:4 (sample:bonded phase). Typically, 0.5–2 g sample is used.
Sample + bonded phase placed in a glass mortar and ground with the pestle.
Homogenized sample + bonded phase placed in MSPD column and eluted with an appropriate solvent e.g. methanol.
Collection of analyte-containing solvent.
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator) or SPE.
Analysis: GC or HPLC.

Figure 9 Matrix solid-phase dispersion.

(SFE), pressurized microwave-assisted extraction (pMAE), atmospheric microwave-assisted extraction (aMAE), pressurized fluid extraction (PFE) or accelerated solvent extraction (ASE), ultrasonic extraction, shake-flask extraction and matrix solid phase dispersion (MSPD). Method development approaches for each extraction technique are shown in **Figures 3–10.**

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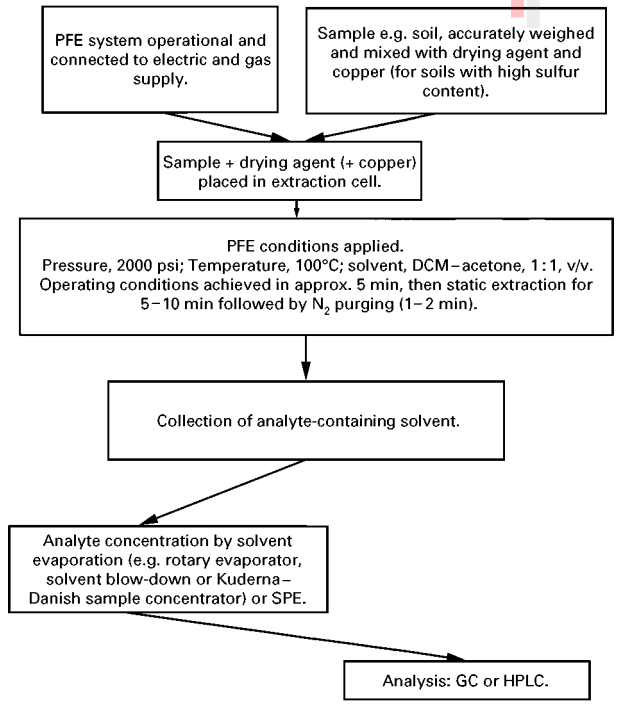
PFE system operational and connected to electric and gas supply.
Sample e.g. soil, accurately weighed and mixed with drying agent and copper (for soils with high sulfur content).
Sample + drying agent (+ copper) placed in extraction cell.
PFE conditions applied.
Pressure, 2000 psi; Temperature, 100°C; solvent, DCM–acetone, 1:1, v/v.
Operating conditions achieved in approx. 5 min, then static extraction for 5–10 min followed by N_2 purging (1–2 min).
Collection of analyte-containing solvent.
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator) or SPE.
Analysis: GC or HPLC.

Figure 8 Pressurized fluid extraction (or accelerated solvent extraction).

Liquid Matrices

Liquid extraction approaches are essentially centred around methods of preconcentration. Typically, this involves the use of sorbent and/or an organic solvent. The choice of solvent/organic solvent depending upon the nature of the analyte, e.g. polar/nonpolar. The main extraction approaches are liquid–liquid

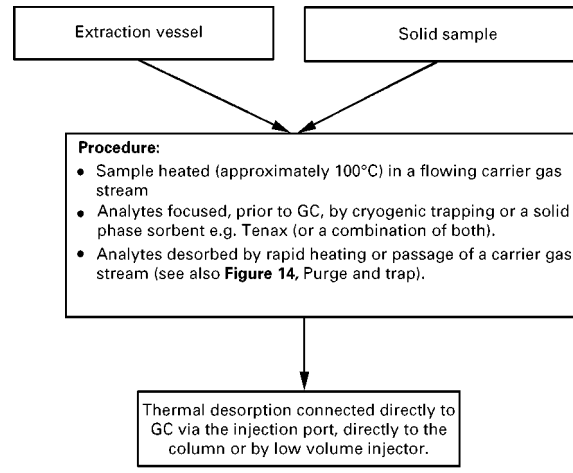
Extraction vessel
Solid sample
Procedure:
• Sample heated (approximately 100°C) in a flowing carrier gas stream
• Analytes focused, prior to GC, by cryogenic trapping or a solid phase sorbent e.g. Tenax (or a combination of both).
• Analytes desorbed by rapid heating or passage of a carrier gas stream (see also Figure 14, Purge and trap).
Thermal desorption connected directly to GC via the injection port, directly to the column or by low volume injector.

Figure 10 Thermal desorption.

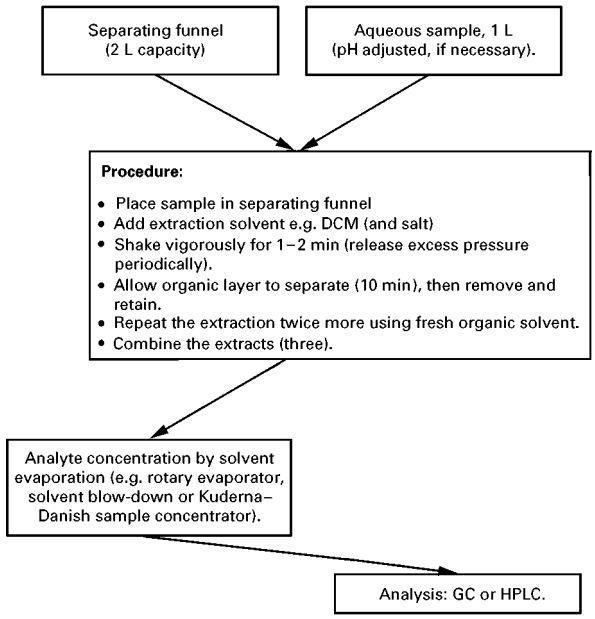
Separating funnel
(2 L capacity)
Aqueous sample, 1 L
(pH adjusted, if necessary).
Procedure:
• Place sample in separating funnel
• Add extraction solvent e.g. DCM (and salt)
• Shake vigorously for 1–2 min (release excess pressure periodically).
• Allow organic layer to separate (10 min), then remove and retain.
• Repeat the extraction twice more using fresh organic solvent.
• Combine the extracts (three).
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator).
Analysis: GC or HPLC.

Figure 11 Separating funnel liquid–liquid extraction.

extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME). A guide to method development for each extraction technique is shown in **Figures 11–14**.

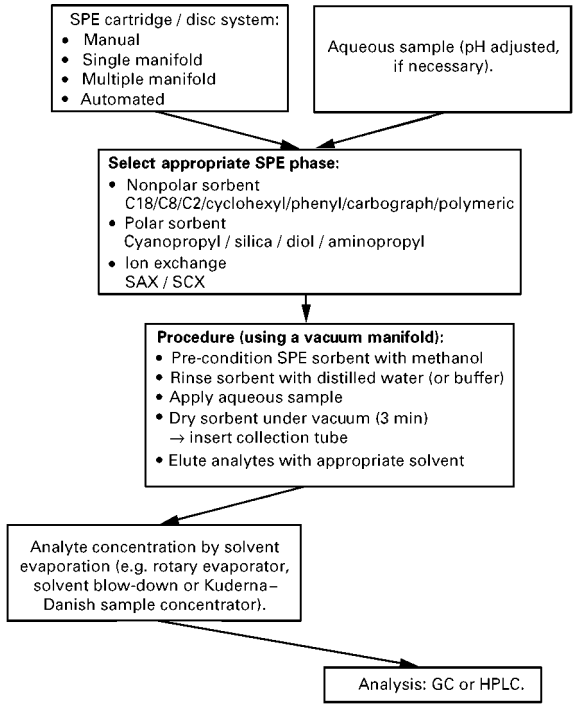
SPE cartridge / disc system:
• Manual
• Single manifold
• Multiple manifold
• Automated
Aqueous sample (pH adjusted, if necessary).
Select appropriate SPE phase:
• Nonpolar sorbent
C18/C8/C2/cyclohexyl/phenyl/carbograph/polymeric
• Polar sorbent
Cyanopropyl / silica / diol / aminopropyl
• Ion exchange
SAX / SCX
Procedure (using a vacuum manifold):
• Pre-condition SPE sorbent with methanol
• Rinse sorbent with distilled water (or buffer)
• Apply aqueous sample
• Dry sorbent under vacuum (3 min)
→ insert collection tube
• Elute analytes with appropriate solvent
Analyte concentration by solvent evaporation (e.g. rotary evaporator, solvent blow-down or Kuderna–Danish sample concentrator).
Analysis: GC or HPLC.

Figure 12 Solid-phase extraction.

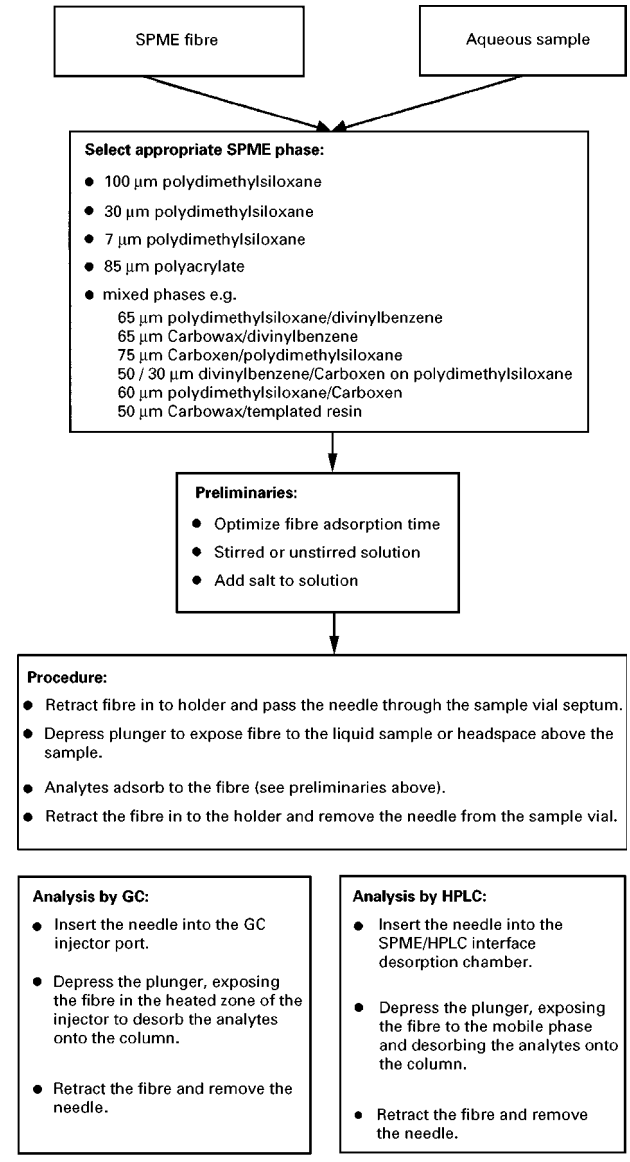
SPME fibre
Aqueous sample
Select appropriate SPME phase:
• 100 μm polydimethylsiloxane
• 30 μm polydimethylsiloxane
• 7 μm polydimethylsiloxane
• 85 μm polyacrylate
• mixed phases e.g.
65 μm polydimethylsiloxane/divinylbenzene
65 μm Carbowax/divinylbenzene
75 μm Carboxen/polydimethylsiloxane
50 / 30 μm divinylbenzene/Carboxen on polydimethylsiloxane
60 μm polydimethylsiloxane/Carboxen
50 μm Carbowax/templated resin
Preliminaries:
• Optimize fibre adsorption time
• Stirred or unstirred solution
• Add salt to solution
Procedure:
• Retract fibre in to holder and pass the needle through the sample vial septum.
• Depress plunger to expose fibre to the liquid sample or headspace above the sample.
• Analytes adsorb to the fibre (see preliminaries above).
• Retract the fibre in to the holder and remove the needle from the sample vial.
Analysis by GC:
• Insert the needle into the GC injector port.
• Depress the plunger, exposing the fibre in the heated zone of the injector to desorb the analytes onto the column.
• Retract the fibre and remove the needle.
Analysis by HPLC:
• Insert the needle into the SPME/HPLC interface desorption chamber.
• Depress the plunger, exposing the fibre to the mobile phase and desorbing the analytes onto the column.
• Retract the fibre and remove the needle.

Figure 13 Solid-phase microextraction.

Gaseous/Atmospheric Samples

Gaseous samples are normally analysed by gas chromatography (GC). The volatile nature of the analytes means that some form of trapping is required. Typical approaches for analyte trapping are shown in **Table 1**.

Solvent Selection

Extraction of an analyte is dependent upon overcoming any interactions between the matrix with the extraction technique. These interactions, for organic molecules, are predominantly based on weak forces of attraction between the analyte and the matrix, e.g.

Table 1 Common approaches for gaseous samples

Technique	*Comments*
Solid phase trapping	Gaseous sample passed through a sorbent, e.g. Tenax, activated charcoal, etc. Trapped analytes are eluted with a suitable solvent.
Liquid trapping	Gaseous sample is bubbled through a suitable trapping solvent. To improve trapping efficiency it is important to minimize the flow rate and/or lower the temperature. The use of multiple traps or impingers may be necessary.
Headspace sampling	Solid or liquid sample placed in a sealed glass vial until equilibrium is reached. Volatile analytes sampled from the headspace using a gas-tight syringe or solid-phase microextraction.
Purge and trap	See Figure 14.
Solid-phase microextraction	See Figure 14 and Headspace sampling, above.

Table 2 Calculation of individual group contributions for a solvent (methanol) and the analyte, DDT

Molecule	*Group*	*Group contribution to dispersion* (F_d) $J^{1/2}\ cm^{3/2}\ mol^{-1}$	*Group contribution to polarity* (F_p) $J^{1/2}\ cm^{2}\ mol^{-1}$	*Group contribution to hydrogen bonding* (U_h) $J\ mol^{-1}$	*Molar volume* (V) $cm^3\ mol^{-1}$
Methanol	CH_3	420	0	0	33.5
	OH	210	500	20 000	10.0
	Total	630	500	20 000	43.5
DDT	2 × -Ph-	2540	220	0	104.8
	2 × Cl-CH=	900	1100	800	48
	3 × Cl	1350	1650	1200	72
	1 × CH	80	0	0	− 1.0
	> C <	− 70	0	0	− 19.2
	Total	4800	2970	2000	204.6

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Table 3 Total Hildebrand solubility parameter and its individual components

Solvent/analyte	*Dispersion coefficient*, δ_d ($MPa^{1/2}$)	*Polarity*, δ_p ($MPa^{1/2}$)	*Hydrogen bonding*, δ_h ($MPa^{1/2}$)	*Total Hildebrand solubility parameter*, δ_t ($MPa^{1/2}$)
Methanol	14.48	11.49	21.44	28.31
Acetonitrile	14.78	19.13	6.59	25.06
Acetone	14.52	9.90	5.07	18.29
Dichloromethane	18.25	8.58	3.53	20.48
iso-Hexane	14.27	0.00	0.00	14.27
DDT	23.46	9.75	3.13	25.60

Van der Waal's, hydrogen bonding, etc. While the choice of extraction technique is important, often for economic and environmental concerns, its physical/chemical properties are largely influenced by the choice of solvent (in most cases). This is not to say that the effects of heat, pressure, agitation and sorbent are negligible, but that these on their own are largely unimportant without the presence of an organic solvent and that the choice of solvent is critical. Apart from general rule of thumb guidelines for solvent selection, i.e. like extracts such as a nonpolar analyte can be extracted by a nonpolar solvent, little attempt has been made to offer a scientific approach.

The solvent prediction scheme used is based on the Hildebrand solubility parameter (δ_t). The solubility parameter is a measure of the internal energy of cohesion in the solvent/solute. Solvents with similar solubility parameter form mixtures, hence an analyte and a solvent that have similar solubility parameters, should also form mixtures.

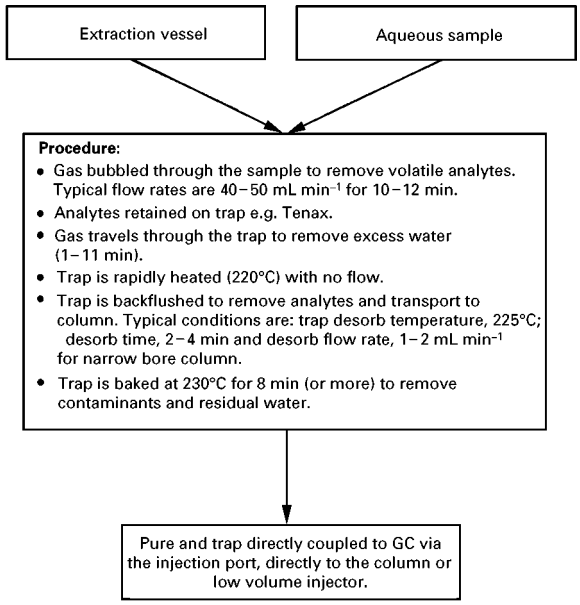

Extraction vessel
Aqueous sample
Procedure:
• Gas bubbled through the sample to remove volatile analytes. Typical flow rates are 40–50 mL min⁻¹ for 10–12 min.
• Analytes retained on trap e.g. Tenax.
• Gas travels through the trap to remove excess water (1–11 min).
• Trap is rapidly heated (220°C) with no flow.
• Trap is backflushed to remove analytes and transport to column. Typical conditions are: trap desorb temperature, 225°C; desorb time, 2–4 min and desorb flow rate, 1–2 mL min⁻¹ for narrow bore column.
• Trap is baked at 230°C for 8 min (or more) to remove contaminants and residual water.
Pure and trap directly coupled to GC via the injection port, directly to the column or low volume injector.

Figure 14 Purge and trap.

δ_t is defined as the square root of the cohesive energy density or:

$$\delta_t = (\Delta E_v/V)^{1/2} \quad [1]$$

where δ_t = total Hildebrand solubility parameter, ΔE_v = energy of vaporization at a given temperature and V = molar volume of the molecule.

Hansen (1967) took this work further and assumed that the total cohesive energy is a linear addition of

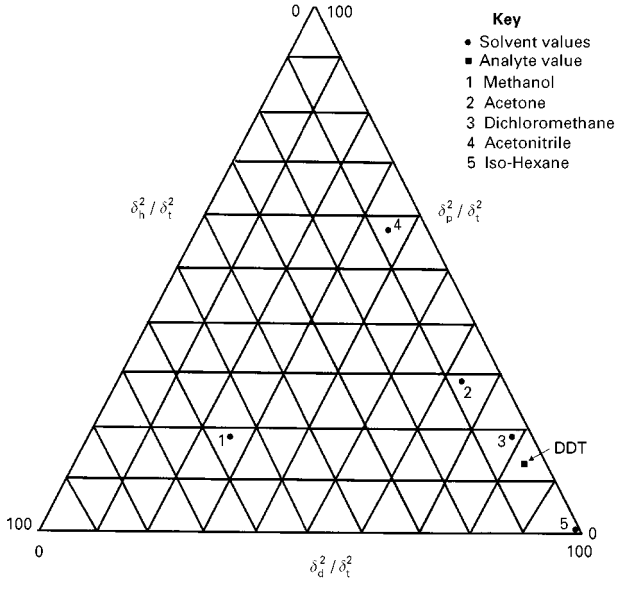


Figure 15 Comparison of calculated solvent and analyte fractional parameters.

Table 4 Pressurized fluid extraction of DDT from contaminated soil followed by GC-MSD quantitation, $n = 6$[a]

Solvent	*Mean* $\mu g\, g^{-1}$	*SD*
Methanol	89	10.1
Acetone	163	7.4
Dichloromethane	220	13.9
Acetonitrile	65	2.9
Iso-Hexane	120	4.4

[a]Extraction conditions: sample size 2 g; temperature, 100°C; pressure 2000 psi; static extraction time 10 min; one static/flush cycle.

three components: δ_h, hydrogen bonding ability contribution; δ_d, dispersion co-efficient contribution; and, δ_p, polarity contribution. They are linked by the following equation:

$$\delta_t^2 = \delta_h^2 + \delta_p^2 + \delta_d^2 \quad [2]$$

The individual components of δ_t can be determined using a group contribution additive method. The data available allows each group's contribution to polarity, dispersion and hydrogen bonding (F_p, F_d, and U_h, respectively) to be calculated using the following equations δ_p, δ_h, and δ_d:

$$\delta_d = ({}_z\Sigma^z F_d)/V \quad [3]$$

$$\delta_p = ({}_z\Sigma^z F_p)/V \quad [4]$$

$$\delta_p = ({}_z\Sigma^z F_p^2)^{1/2}/V \quad [5]$$

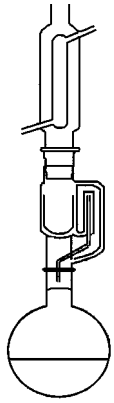
$$\delta_h = (({}_z\Sigma^z U_h)/V)^{1/2} \quad [6]$$

For molecules with more than one polar group present, then eqn [5] must be used instead of eqn [4] to take into account the interactions between the polar groups.

An example calculation of the individual components of the solubility parameter for a solvent (methanol) and an analyte (1,1,1-trichloro-2-2-bis(p-chlorophenyl)ethane (DDT)) are shown in **Table 2**. The individual Hansen parameters for a range of solvents and an analyte (DDT) are shown in **Table 3**. As an example, the calculated total Hildebrand solubility parameter, δ_t, for methanol (28.3 $MPa^{1/2}$) compared favourably with the literature value of 29.6 $MPa^{1/2}$.

In order to normalize the data, fractional parameters of the Hildebrand solubility parameter can be calculated and plotted on a triangular graph in order to give a visual representation of the extent of contribution from the three components (polarity,

Box 1 Soxhlet extraction of polycyclic aromatic hydrocarbons from contaminated soil.

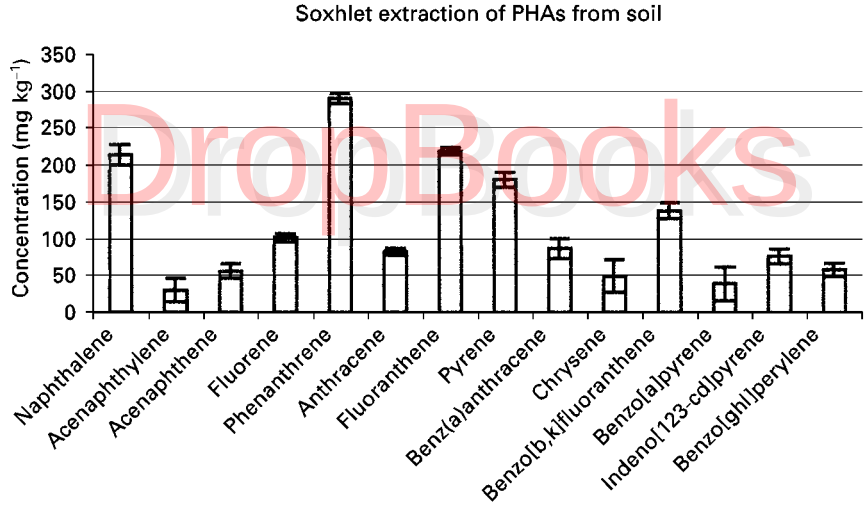


Extraction conditions
Sample size: 10 g plus 10 g anhydrous sodium sulfate
Solvent: 150 mL dichloromethane
Extraction time: 24 h

Comments: sample heated using an isomantle. Typically, refluxing of solvent occurs at the rate of 4 h^{-1}. Extracts were concentrated to 10 mL using rotary evaporator and then diluted twofold before addition of the internal standards.

Analysis of extracts by GC
Separation and identification of individual PAHs was done on a HP 5890 series II + GC fitted with a HP 5972A mass spectrometer. A 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 capillary column was used with temperature programming from an initial temperature held at 85°C for 2 min before commencing a 6°C min^{-1} to 300°C, with a final time of 7 min. The split/splitless injector was held at 300°C and operated in splitless mode with the split value closed for 1 min following sample injection. The split flow was set at 40 mL min^{-1}, and the mass spectrometer transfer line was maintained at 270°C. Electron impact ionization at 70 eV with an electron multiplier voltage set at 1500 V was used while operating in single-ion monitoring (SIM) mode.

Typical results: Saim N, Dean JR, Abdullah MP and Zakaria Z (1997) *Journal of Chromatography* 791A: 361.



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dispersion and hydrogen bonding). A plot of selected solvents and DDT is shown in **Figure 15**. Using this plot, it can be seen that dichloromethane (DCM) is predicted to be the optimum solvent for extraction of DDT. **Table 4** shows results for the extraction of DDT contaminated soil for selected solvents using accelerated solvent extraction (ASE). It is clearly shown that DCM gives the highest recovery of DDT. Similarly, it is also predicted and confirmed that both isohexane and acetone would remove significantly more of the DDT than methanol and acetonitrile. Work is on-going to identify whether the model can be applied to other systems.

Selected Examples of Extraction of Analytes from Environmental Matrices

In order to provide specific details on particular extraction techniques selected examples are provided from the author's own laboratory. In particular, the following techniques are covered: **Box 1**, Soxhlet extraction of polyaromatic hydrocarbons (PAHs) from contaminated soil; **Box 2**, shake flask extraction of four phenols from soil; **Box 3**, SFE of OCPs from soil and Celite; **Box 4**, pressurized microwave-assisted extraction of PAHs from soil; **Box 5**, atmospheric microwave-assisted extraction of PAHs from

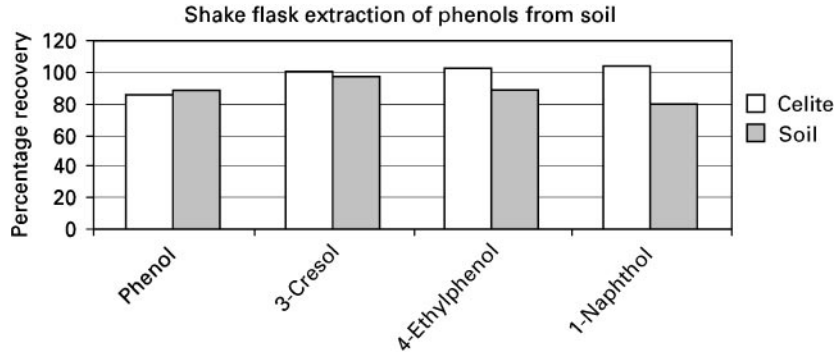
Box 2 Shake flask extraction of phenols from soil

Extraction conditions
Sample size: 1 g
Solvent: 50 mL methanol–water (60–40% v/v)
Extraction time: 30 min

Comments: Sample and solvent placed in a 100 mL screw-capped bottle and extracted on a rotating disc Warburg mixer. Resultant sample/solvent was filtered under vacuum. Sample extracted filtered through a 0.45 μm membrane Acrodisk prior to analysis.

Analysis by HPLC
Separation and quantification was achieved using a 25 cm × 4.6 mm i.d. ODS2 column with UV detection at 275 nm. The mobile phase was operated under isocratic conditions acetronitrile–H_2O–acetic acid (40 + 59 + 1) at a flow rate of 1 mL min^{-1}. A 20 μL Rheodyne injection loop was used to introduce samples and standards on to the column (30°C).

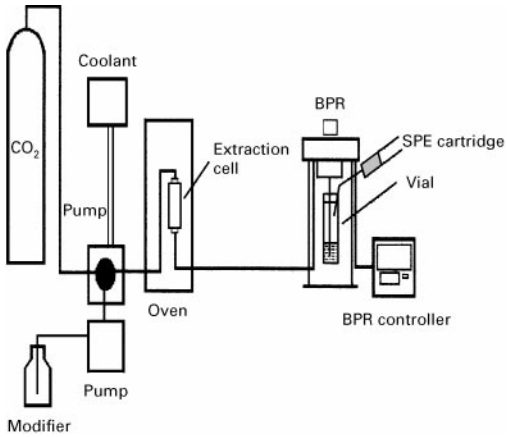
Typical results: Hancock P and Dean JR (1997) *Analytical Communications* 34: 377.



soil; **Box 6**, pressurized fluid extraction of DDT, 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (DDD) and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE) from soil; **Box 7**, liquid–liquid extraction of PAHs from water; **Box 8**, SPE of phenols from water; **Box 9**, solid-phase microextraction of benzene, toluene, ethyl benzene and xylene (BTEX) from water; and, **Box 10**, purge and trap of BTEX from water.

Further details on the theoretical and technical aspects of these and other extraction techniques can be found in the relevant entries in the Encyclopedia.

Box 3 Supercritical fluid extraction of organochlorine pesticides from soil and Celite

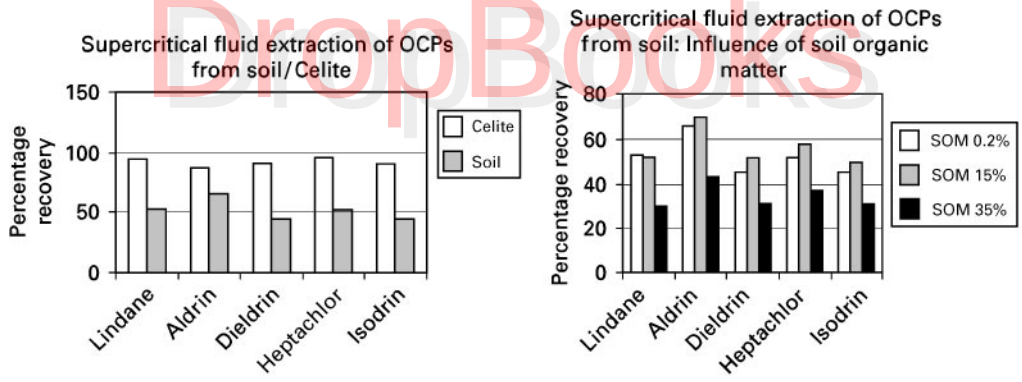


Extraction conditions
Sample size: 1 g
SFE conditions: pressure, 250 kg cm^{-2}; temperature, 50°C; static extraction time, 15 min followed by 40 min dynamic extraction time; and a flow rate of liquid CO_2, 2 mL min^{-1}.

Comments: Extracts collected in a vial containing 3–4 mL DCM. Escaping CO_2 and analytes vented through a C18 SPE cartridge which was back-flushed with 1–2 mL methanol after each extraction.

Analysis by GC
Separation and identification of individual OCPs was done on a HP 5890 series II + GC fitted with a HP 5972A mass spectrometer. A 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5 capillary column was used with temperature programming from an initial temperature held at 85°C for 0.75 min before commencing a 16°C min^{-1} to 285°C, with a final time of 2 min. The split/splitless injector was held at 280°C and operated in splitless mode with the split valve closed for 1 min following sample injection. The split flow was set at 40 mL min^{-1}, and the mass spectrometer transfer line was maintained at 290°C. Electron impact ionization at 70 eV with an electron multiplier voltage set at 1500 V was used while operating in single-ion monitoring (SIM) mode.

Typical results: Dean JR, Barnabas IJ and Owen SP 1996 *Analyst* 121: 465.



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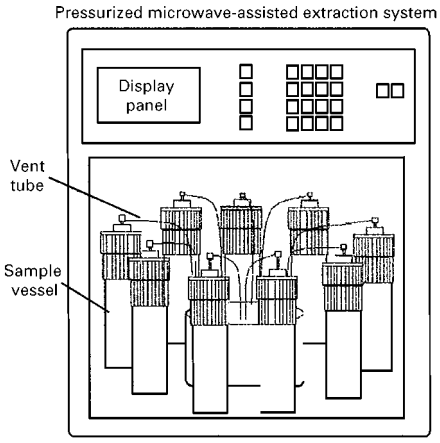
Box 4 Pressurized microwave-assisted extraction of polycyclic aromatic hydrocarbons (PAHs) from soil.

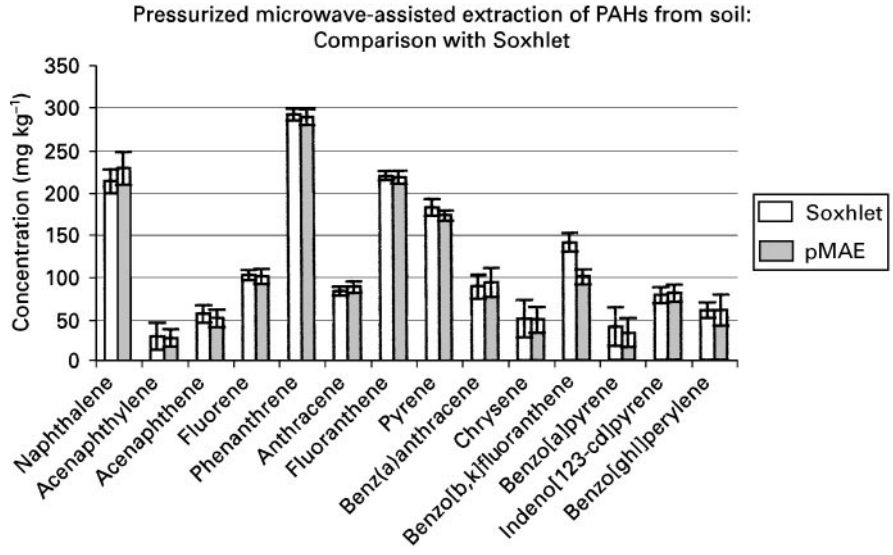


Extraction conditions
Sample size: 2 g
Solvent: 40 mL acetone
pMAE conditions: power, 30% (for a 950 W system); temperature, 120°C; extraction time, 20 min.

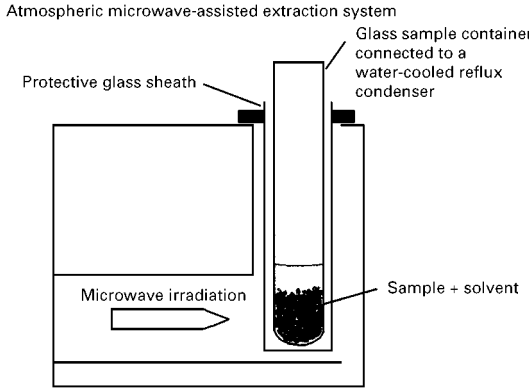
Comments: After extraction, extraction vessels allowed to cool. Contents of vessels were then filtered through a GF/A glass microbore filter. Extracts were concentrated to 5 mL using a rotary evaporator before addition of internal standards.

Analysis by GC
Separation and identification of individual PAHs was done on a Carlo Erba HRGC 5300 Mega Series with on-column injection and flame ionization detection. A 30 m × 0.32 mm i.d. × 0.1 μm film thickness DB-5 HT capillary column was used with temperature programming from an initial temperature held at 50°C for 2 min before commencing a 15°C min^{-1} to 90°C; hold for 2 min; increase at 6°C min^{-1} to 300°C with a final hold time of 8 min. The detector temperature was set at 290°C.

Typical results: Saim N, Dean JR, Abdullah MP and Zakaria Z (1997) *Journal of Chromatography* 791A: 361, with permission from Elsevier Science.



Box 5 Atmospheric microwave-assisted extraction of polycyclic aromatic hydrocarbons (PAHs) from soil.

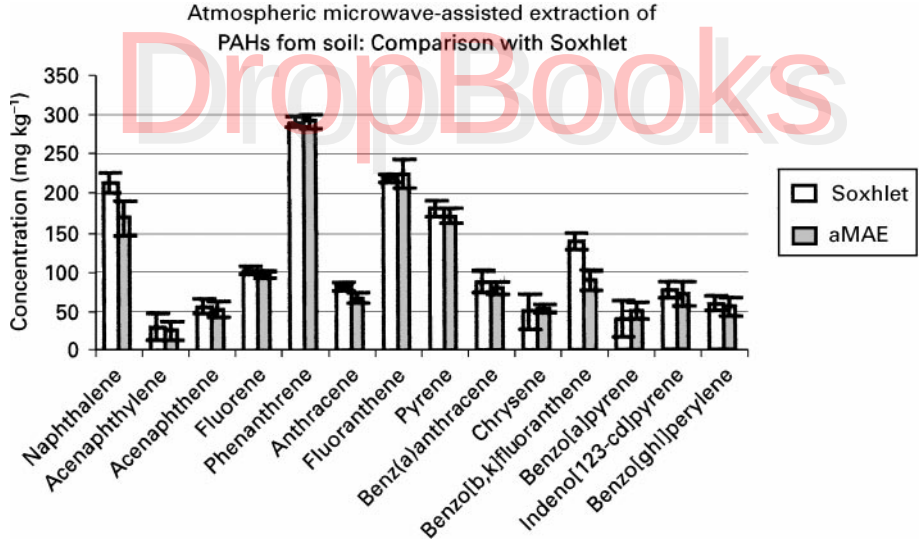

Atmospheric microwave-assisted extraction system
Glass sample container connected to a water-cooled reflux condenser
Protective glass sheath
Microwave irradiation
Sample + solvent

Extraction conditions
Sample size: 2 g
Solvent: 70 mL DCM
pMAE conditions: power, 99% (for a 300 W system); extraction time, 20 min.

Comments: Contents of extraction vessel was then filtered through a GF/A glass microbore filter. Extracts were concentrated to 5 mL using a rotary evaporator before addition of internal standards.

Analysis by GC
Separation and identification of individual PAHs was done on a Carlo Erba HRGC 5300 Mega Series with on-column injection and flame ionization detection. A 30 m × 0.32 mm i.d. × 0.1 μm film thickness DB-5 HT capillary column was used with temperature programming from an initial temperature held at 50°C for 2 min before commencing a 15°C min^{-1} to 90°C; hold for 2 min; increase at 6°C min^{-1} to 300°C with a final hold time of 8 min. The detector temperature was set at 290°C.

Typical results: Saim N, Dean JR, Abdullah MP and Zakaria Z (1997) *Journal of Chromatography* 791A: 361, with permission from Elsevier Science.



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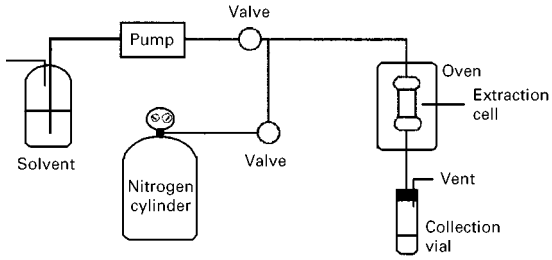
Box 6 Pressurized fluid extraction of DDT, DDD and DDE from soil.

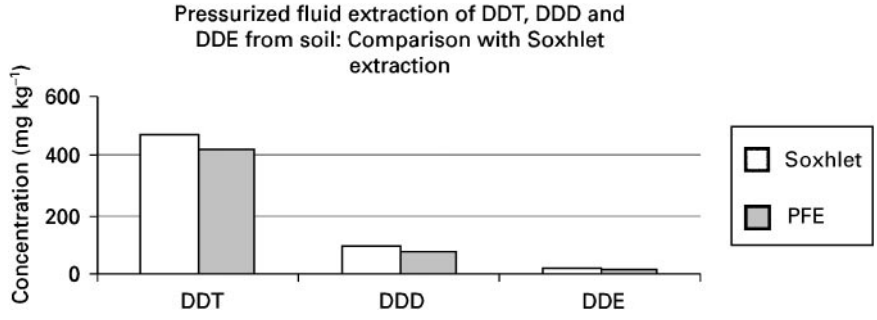


Extraction conditions
Sample size: 2 g
PFE conditions: pressure, 2000 psi; temperature, 100°C; static extraction time, 10 min; and three static/flush cycles.

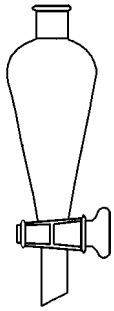
Comments: Sample placed in stainless steel extraction cell on top of a filter to prevent cell frit blockage. Hydromatix was used to fill the headspace to reduce solvent consumption.

Analysis by GC
Separation and identification of DDT, DDD and DDE was done on a HP 5890 series II + GC fitted with a HP 5972A mass spectrometer. A 30 m × 0.25 mm i.d. × 0.25 μm film thickness DB-5ms capillary column was used with temperature programming from an initial temperature held at 120°C for 2 min before commencing at 5°C min^{-1} to 290°C, with a final time of 2 min. The split/splitless injector was held at 280°C and operated in splitless mode. The mass spectrometer transfer line was maintained at 280°C. Electron impact ionization at 70 eV with an electron multiplier voltage set at 1500 V was used while operating in single-ion monitoring (SIM) mode.

Typical results: Fitzpatrick LJ and Dean JR (2000) *Journal of Chromatography*, in press.



Box 7 Liquid–liquid extraction of polyaromatic hydrocarbons (PAHs) from water

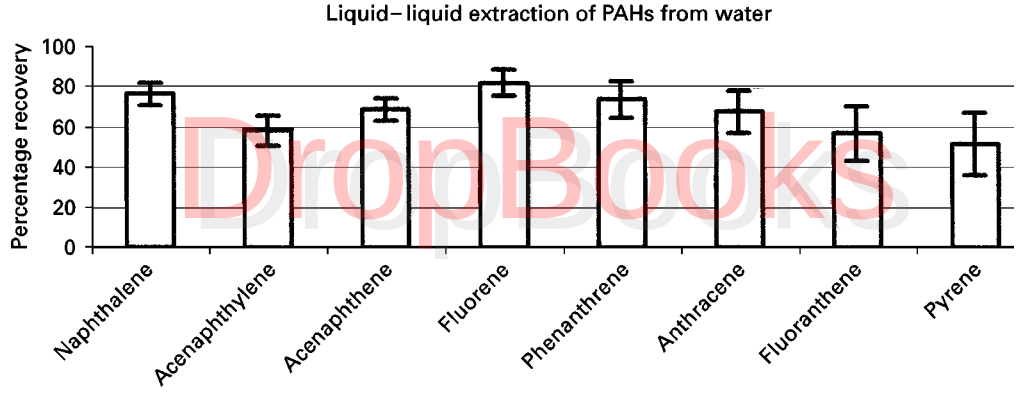


Extraction conditions
Sample volume: 25 mL
LLE conditions: sample extracted with 2×3 mL of DCM plus 1 g salt (NaCl). Each extract was shaken for 5 min each.

Comments: Combined extracts placed in a volumetric flask, internal standard added, prior to analysis.

Analysis by GC
Separation and identification of individual PAHs was done on a HP 5890 series II GC fitted with a HP 5971A mass spectrometer. A 30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm film thickness HP-5ms capillary column was used with temperature programming from an initial temperature held at 90°C for 2 min before commencing a 7°C min^{-1} to 285°C, with a final time of 20 min. The split/splitless injector was held at 280°C and operated in splitless mode with the split valve closed for 1 min following sample injection. The split flow was set at 40 mL min^{-1}, and the mass spectrometer transfer line was maintained at 280°C. Electron impact ionization at 70 eV with an electron multiplier voltage set at 1500 V was used while operating in single-ion monitoring (SIM) mode.

Typical results: Arenaz-Laborda MP (1998) MSc dissertation, University of Northumbria at Newcastle, UK.



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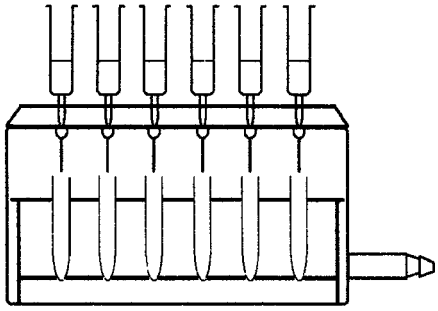
Box 8 Solid phase extraction of phenols from water.



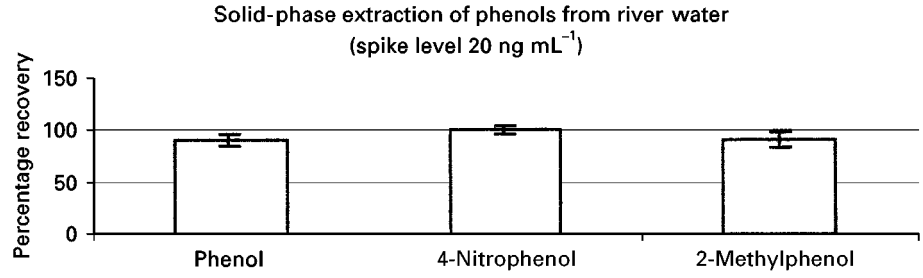
Extraction conditions
Sample volume: 25 mL
SPE sorbent: PS-DVB, 230 mg
SPE conditions: conditioning, 5 mL of acetonitrile followed by 5 mL of water; sample loading; interference elution, 2 mL of water; and analyte elution, 4 mL of acetonitrile.

Comments: sample extract made up to 10 mL with water.

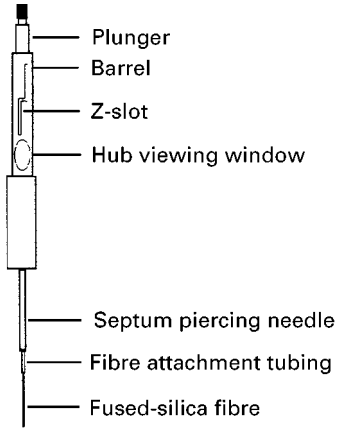
Analysis by HPLC
Separation and quantitation was achieved using a 25 cm $\times$ 4.6 mm id ODS2 column with UV detection at 275 nm. The mobile phase was operated under isocratic conditions acetonitrile–H_2O–acetic acid (40 + 59 + 1) at a flow rate of 1 mL min^{-1}. A 100 μL Rheodyne injection loop was used to introduce samples and standards on to the column (35°C).

Typical results: Madier C (1997) BSc project, UNN, Newcastle upon Tyne, UK.

Analysis of phenol, 4-nitrophenol and 2-methylphenol.
Calibration range: 0–400 ng mL^{-1}
Correlation coefficients: 0.9993–0.9979.



Box 9 Solid phase microextraction of BTEX from water.

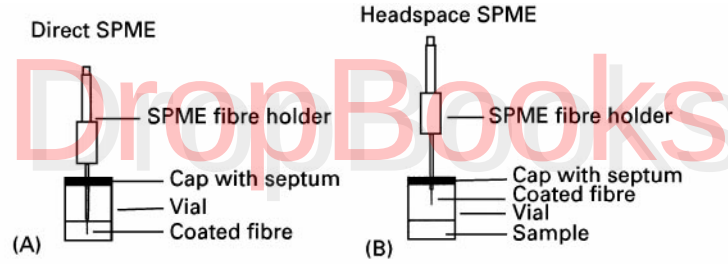


Extraction conditions
Sample volume: 10 mL
Fibre: 100 μm polydimethylsiloxane

Conditions: SPME: fibre inserted into either the sample or headspace above the sample (with/without stirring; with/without salt) for varying amounts of time.

Analysis by GC
Separation and identification of BTEX was done on a Carlo Erba HRGC 5300 Mega Series with split/splitless injection and flame ionization detection. A 30 m × 0.25 mm i.d. × 0.1 μm film thickness DB-5 capillary column was used with temperature programming from an initial temperature held at 50°C for 3 min before commencing a 16°C min^{-1} to 120°C with a final hold time of 7 min. The detector temperature was set at 250°C.

Typical results: Ahmed HK (1996) MSc dissertation, University of Northumbria at Newcastle, UK.



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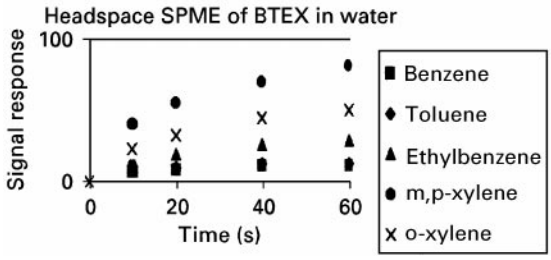
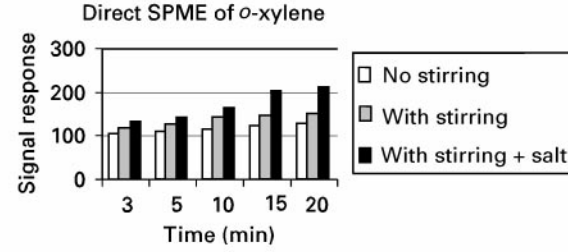
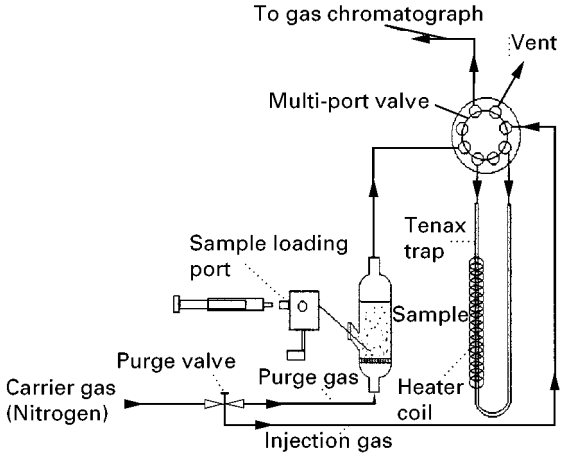




Box 10 Purge and trap (P&T) of BTEX from water.

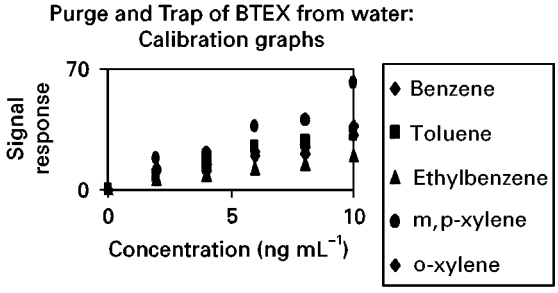


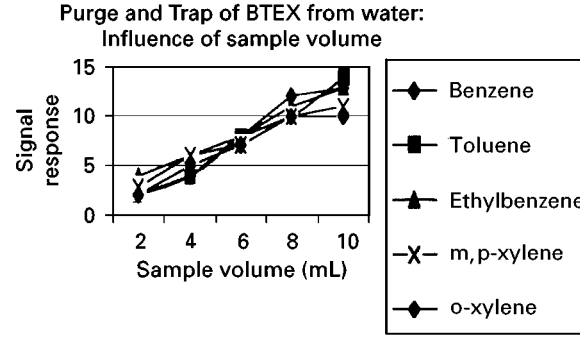
Extraction conditions
Sample volume: 2–10 mL
P&T conditions: Sample sparged for 2–5 min using N_2.
BTEXs trapped on Tenax trap maintained at 20°C for 1–5 min.
Analytes desorbed by rapid heating to 260°C for 1 min.

Comments: GC column initially maintained at 50°C to concentrate analytes.

Analysis by GC
Separation and identification of BTEX was done on a Carlo Erba HRGC 5300 Mega Series with split/splitless injection and flame ionization detection. A 30 m × 0.25 mm i.d. × 0.1 μm film thickness DB-5 capillary column was used with temperature programming from an initial temperature held at 50°C for 3 min before commencing a 16°C min^{-1} to 120°C with a final hold time of 7 min. The detector temperature was set at 250°C.

Typical results: Ahmed HK (1996), MSc dissertation, University of Northumbria at Newcastle, UK.





See also: **I/Extraction; Chromatography: Thin-Layer (Planar):** Theory of Thin-Layer (Planar) Chromatography. **Extraction:** Analytical Extractions; Analytical Inorganic Extractions; Microwave-Assisted Extraction; Solid-Phase Extraction; Solid-Phase Microextraction; Solvent Based Separation; Steam Distillation; Supercritical Fluid Extraction; Ultrasound Extractions. **III/Airborne Samples: Solid-Phase Extraction. Bioanalytical Applications: Solid-Phase Extraction. Drugs of Abuse: Solid-Phase Extraction. Environmental Applications:** Solid-Phase Microextraction; Soxhlet Extraction; Supercritical Fluid Extraction. **Herbicides:** Solid-Phase Extraction. **Immobilised Boronic Acids: Extraction. Immunoaffinity Extraction. Molecular Imprints for Solid-Phase Extraction. Multiresidue Methods: Extraction. On-line Sample Preparation: Supercritical Fluid Extraction. Pesticides:** Extraction from Water. **Phenols:** Solid-Phase Extraction. **Pressurized Fluid Extraction: Non-Environmental Applications. Solid-Phase Extraction with Discs. Sorbent Selection for Solid-Phase Extraction. Appendix: 2/Essential Guides to Method Development in Solid-Phase Extraction.**

Further Reading

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ESSENTIAL GUIDES TO METHOD DEVELOPMENT IN FLOTATION

E. Woodburn, UMIST, Manchester, UK

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General

This article is designed to develop methods for an interested non-specialist, by showing how they can be used as a basis for a Chemical Engineering Unit Operations course.

Flotation is practised extensively in industry. The technique requires a detailed knowledge in physical metallurgy, the physical chemistry of surfaces, a competence both in mathematics and practical hydrodynamics.

The operation is based simply on the attachment of an air bubble to either a small or low-density particle, or to a liquid droplet.

PrepBooks

Method 1: Selective Separation

Mineral flotation has by far the greatest usage, processing 20 billion tons per year; however the process of delinking newsprint is currently at about 25 million tons per year and is expected to grow significantly in the next decade. In these operations the selective attachment of a bubble to the valuable or an unwanted component of a particle is required. In de-inking, this refers to the removal of ink particles from cellulosic fibres. For mineral processing, a higher degree of selectivity is required, to recover a valuable particle from a suspension of waste particles. This operation is very seldom used on its own but is part of a flowsheet in which, after pretreatment which includes size reduction, a solid suspension in water is fed to the flotation circuit.

In the circuit, cells may be arranged in sequence with each successive cell treating the concentrate from the previous one to improve its purity; this is, called 'roughing'. The final concentrate from the rougher bank is fed to a bank of 'cleaning' cells. The reject stream from the last of the cleaning cells is itself recycled to improve the final recovery and is called 'scavenging'. The concentrate from the final scavenger stream is recirculated to the feed of the first of the rougher cells. The waste from the final scavenging cell is discharged as the overall plant waste. This may be recycled, or treated to minimize its environmental impact. The final cleaner concentrate is essentially the plant product, although it may also have to be processed possibly by recleaning and drying.

In waste paper, de-inking the ink-rich stream tailings appears in what in mineral processing is the concentrate and the de-inked paper in what is usually the mineral processing tailings.

Method 2: Non-Selective Separations

The other class of operations require only the non-selective attachment of air bubbles to a particle/droplet, producing an aggregate of high buoyancy, so that the attached material can be withdrawn from the top of the flotation vessel. Processes of this type include the off-shore recovery of crude oil which may be 5–50% oil by volume, containing dispersed oil in the form of 10–50 μm oil droplets in water. After processing, virtually all the oil is recovered containing only 0–5% water. Other processing operations of this class include water treatment, in which the rate of setting of the flocculants on their own is very slow while the buoyancy of the air bubble/flocculant is high. Also the separation of rejected plastics from general wastes is economically attractive, with polyethylene terephthalate (PET), polyethylene (PE),